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Arsenic Speciation Including 'Hidden' Arsenic in Natural Waters

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Recent studies indicate the existence in natural waters of 'hidden' arsenic which had previously been undetected by hydride generation technique. A speciation method for arsenic species has been developed in which hidden arsenic was classified into two fractions by their lability to the photochemical degradation procedure: the ultraviolet-labile fraction and the ultraviolet-resistant fraction. We discussed the hidden arsenic fraction as the key to explaining arsenic speciation in natural waters.

Keywords : Arsenic/Speciation/Organoarsenicals/Ultraviolet irradiation/Microwave digestion/Arsenic methylation/Natural water

Chemical speciation is the determination of the individual concentrations of the various forms of an element that together make up the total concentration of that element. So far as arsenic species in natural waters are concerned, the inorganic forms (arsenate $[\text{AsO}(\text{OH})_3; \text{As(V)}]$ and arsenite $[\text{As}(\text{OH})_3; \text{As(III)}]$) and the methylated forms (methylarsonic acid $[\text{CH}_3\text{AsO}(\text{OH})_2; \text{MMAA(V)}]$ and dimethylarsinic acid $[(\text{CH}_3)_2\text{AsO}(\text{OH}); \text{DMAA(V)}]$) have been reported to be the main species. The bulk of the total dissolved arsenic is inorganic species in seawater and in fresh water, whereas methylarsenicals are found to comprise significant amounts in the surface layers and above the sediment surface. Several observations showed that methylarsenicals in surface waters exhibit a seasonal cycle in which the maximum concentrations of methylarsenicals appear during the summer. Although

there is abundant evidence regarding methylarsenicals produced biologically in natural waters, apparent differences were observed in seasonal changes of phytoplankton densities and methylarsenicals.^{1,2}

On the other hand, other organoarsenicals make up the bulk of the arsenic stock in organisms. Arsenosugars are ubiquitous in algae and arsenobetaine is the predominant form in marine animals. Arsenosugars and arsenobetaine can not be detected with the conventional hydride generation analyses, which have been applied to natural water samples. These facts suggest the presence of additional organoarsenicals that had previously been undetected in natural waters by hydride generation atomic absorption spectrometry. We established the new speciation method for these 'hidden' arsenic species using ultraviolet irradiation and microwave digestion, and studied their applications to estimate the arsenic compo-

INTERFACE SCIENCE — Separation Chemistry —

Scope of research

Our research activities are concerned in the behavior of chemical substances in geochemistry and the biochemical reactions. Major subjects of the research are followings: (1) Biogeochemistry of trace elements in the hydrosphere. Analytical methods for trace elements are developed using the selective complex formation systems. The behavior of trace elements in hydrosphere is explored to realize the significance of them for ecosystem. (2) Design and synthesis of the selective complex formation systems. Ligands (host molecules) that have novel functions in separation of metal ions and guest molecules are designed and synthesized.



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sition in natural waters.³

Hidden arsenic can be classified into different fractions by their lability to the photochemical degradation procedure: the ultraviolet-labile fraction and the ultraviolet-resistant fraction. We estimate the ultraviolet-labile fraction as the increment in measurable arsenic concentration before and after the ultraviolet irradiation, and the ultraviolet-resistant fraction as the difference in measurable arsenic after the ultraviolet irradiation and the microwave digestion. Figure 1 shows typical photoproduction of inorganic and methylarsenic species in ultraviolet-irradiated samples. Initially, both filtered and unfiltered samples contained only inorganic arsenic (9.3 nM and 11.5 nM, respectively), and methylarsenic concentration was below detection limits. Inorganic and dimethylarsenic concentrations rapidly increased immediately after irradiation, and attained equilibrium in 1-3 h. The lake waters as well as other Uranouchi waters also showed similar speciation changes to those described above, although they varied as to their increments in arsenic concentration. The total bulk concentration in natural waters was determined by microwave digestion with added potassium persulphate combined with CT-HG-AAS. Organoarsenicals are decomposed into As(V) by persulphate, and microwave irradiation speeds the oxidative decomposition by its rapid heating ability.

Figure 2 shows the measured arsenic fractions in Uranouchi Inlet and Lake Biwa. UV-InorgAs, UV-MMA, and UV-DMA are the corresponding inorganic, monomethyl, and dimethylarsenic concentration in the ultraviolet-labile fraction. The observed results strongly suggest that hidden arsenic exists in both seawater and in fresh water. Uranouchi Inlet clearly showed higher concentrations of hidden arsenic than Lake Biwa, in spite of the similar composition of the inorganic and methylarsenic fractions. This pattern was consistent with the higher dissolved organic carbon (DOC) of

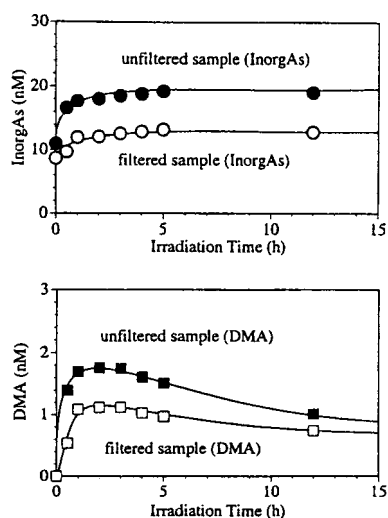


Figure 1. Effect of irradiation time with a 400 W high-pressure mercury lamp on arsenic speciation. Samples were collected from surface waters (depth; 0 m) of Uranouchi Inlet, on April 30, 1997. Monomethylarsenic was below the detection limit by CT-HG-AAS.

Uranouchi Inlet relative to Lake Biwa. The values of DOC were 2-4 mgC/l and <0.3 mgC/l in Uranouchi Inlet and Lake Biwa, respectively. Between filtered and unfiltered samples, the difference of hidden arsenic was significant compared with that of inorganic and methylarsenicals. It is likely that the hidden arsenic in the >0.45 μ m size fraction was derived from the organoarsenicals in biological organic detritus.

The highest concentration of the ultraviolet-resistant fraction was observed on June 23 in Uranouchi Inlet with the highest dimethylarsenic concentration and a lower concentration of the ultraviolet-labile fraction. It appears that the increased dimethylarsenic concentration was due to photodegradation of hidden arsenic by strong sunlight in early summer. However, when exposed to the filtered light above a wavelength of 280 nm from a mercury lamp, both unfiltered samples of seawater and fresh water showed no significant change in the arsenic speciation. It is evident that photoproduction of UV-InorgAs, UV-MMA, and UV-DMA occurred in response only to the ultraviolet region of 250-280 nm when a high-pressure mercury lamp was used as an illuminator. These results indicate that photochemical degradation by sunlight rarely contributes to the production of methylarsenic compounds in natural waters.

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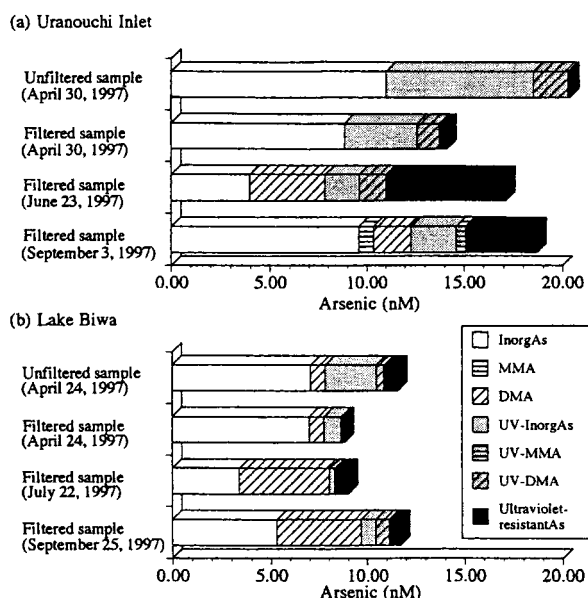


Figure 2. Bar diagram showing the mean concentration and distribution of arsenic in natural waters. Samples were collected from surface waters (depth; 0 m) of (a) Uranouchi Inlet on April 30, 1997, and (b) the southern basin of Lake Biwa on